Supporting Information to:

Synthesis and Stereochemistry of Helical Polyurethanes Based on 2,2'-Dihydroxy-1,1'-binaphthyl and Diisocyanatobenzenes

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Experimental

Materials. 1,4-Diisocyanatobeznene (TCI), 1,3-diisocyanatobenzene (TCI), (*R*)-(+)-1,1'-bi-2-naphthol (TCI), and (*S*)-(-)-1,1'-bi-2-naphthol (TCI) were used as purchased. Tetrahydrofuran (Kanto Chemical) was dried with sodium benzophenone ketyl and distilled immediately before use under N_2. Et_3N was distilled over CaH_2 and stored over KOH under nitrogen.

Synthesis of poly(BINOL-*alt*-14DIB). The synthetic procedure is described for the system with (*R*)-(+)-1,1'-bi-2-naphthol at 50% e.e. is described. To a solution of (*R*)-(+)-1,1'-bi-2-naphthol (0.1 g, 0.35 mmol) in THF (2 mL) were added 1,4-diisocyanatobenzene (0.056 mg, 0.35 mmol) and triethylamine (0.11 mL, 0.79 mmol) in this order under nitrogen atmosphere. The mixture was stirred for 24 h at room temperature and terminated by exposure to air. The polymer and cyclic dimer were isolated and purified by preparative SEC. SEC (vs. standard polystyrenes): M_n 2740, M_w/M_n 1.22. FT-IR (KBr) υ/cm^{-1}: 3405, 3062, 2962, 2923, 2852, 1726, 1610, 1512, 1261, 1191, 1096, 1077, 1033,1015, 803.

Synthesis of Poly(BINOL-*alt*-13DIB). The synthetic procedure is described for the system with (R)-BINOL at 50% e.e. is described. To a solution of (*R*)-(+)-1,1'-bi-2-naphthol (0.1 g, 0.35 mmol) in THF (2 mL) were added 1,3-diisocyanatobenzene (0.056 mg, 0.35 mmol) and triethylamine (0.11 mL, 0.79 mmol) in this order under nitrogen atmosphere. The mixture was stirred for 24 h at room temperature and terminated by exposure to air. The polymer and cyclic dimer were isolated and purified by preparative SEC. SEC (vs. standard polystyrenes): M_n 3430, M_w/M_n 1.24. FT-IR (KBr) υ/cm^{-1}: 3391, 3062, 2922, 1733, 1610, 1535, 1508, 1492, 1471, 1457, 1427, 1359, 1307, 1192, 1076, 1038, 1016, 970, 772, 749.

Film fabrication and annealing. Film samples were prepared from a $CHCl_3$ solution of a polymer by drop-casting on to a quartz plate (1 cm x 2 cm x 0.1 cm).

General instrumentation. ^{1}H NMR spectra were recorded on a JEOL JNM-ECX400 spectrometer (400 MHz for ^{1}H measurement) and a JEOL JNM-ECA600 spectrometer (600 MHz for ^{1}H measurement). SEC measurements were carried out using a chromatographic system consisting of a Hitachi L-7100 chromatographic pump, a Hitachi L-7420 UV detector (254 nm), and a Hitachi L-7490 RI detector equipped with TOSOH TSK gel G6000H_{HR} and G3000H_{HR} columns (30 x 0.72(i.d.) cm) connected in series (eluent THF, flow rate 1.0 mL/min). SEC analyses were also carried out at room temperature using a chromatographic system consisting of a JASCO PU-2080 PLUS intelligent HPLC pump, a JASCO UV-2075 PLUS intelligent UV/Vis detector (254 nm), a JASCO RI-930 intelligent RI detector, and a JASCO CO-1565 intelligent column oven (23 ^{o}C) equipped with TOSOH TSK gel G6000H$_{HR}$ and G3000H$_{HR}$ columns (30 x 0.72(i.d.) cm) connected in series (eluent $CHCl_3$, flow rate 1.0 mL/min). Preparative SEC separation of dimers was performed using a JAI LC-908 preparative recycle chromatograph equipped with JAIGEL-1H and JAIGEL-2H columns connected in series (eluent $CHCl_3$). Chiral HPLC was performed using chromatographic system consisting of a JASCO DG-980-50 degasser, a JASCO PU-980 pump, a JASCO CD-2095plus CD detector, and a JASCO UV-2070plus UV detector equipped with a Daicel Chiral Pak IA column (25 cm x 0.46 cm (i.d.)) [eluent CH_2Cl_2-hexane (95/1), flow rate 0.5 mL/min]. UV-vis absorption spectra were measured at room temperature with a JASCO V-550 and V-570 spectrophotometers. Steady-state emission spectra were taken on a JASCO FP-8500 fluorescence spectrophotometer. IR spectra were recorded on a JASCO FT/IR-6100 spectrometer using KBr pellet samples. Circular dichroism (CD) and linear dichroism (LD) spectra were taken with a JASCO-820 spectrometer. The spectra were obtained by averaging those recorded at four (90^{o} interval) or two (180^{o} interval) different film orientations (angles) with the film face positioned vertically to the incident light beam for measurement. Linear dichroism contributions were thus minimized to afford true CD spectra. Differential scanning calorimetry (DSC) and thermal gravity analysis (TGA) were taken on Rigaku Thermo Plus DSC8230 and TG8120 analyzer at a heating rate of 10 K/min in nitrogen atmosphere. WAXD measurement was performed on a RIGAKU Miniflex diffractometer.

Circularly polarized luminescence (CPL) emission measurements. Circularly polarized luminescence (CPL) measurements were attempted using a JASCO CPL-300 spectrophotometer for film samples.

Crystal structure analysis. Crystal data were collected on a Bruker SMART Apex II CCD diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) at 90 K. The crystal structures were solved by direct methods (SHELXS-2013)[1] and refined by full-matrix least-squares methods on F^2 (SHELXL-2014)[2] with APEX II software. The carbon and oxygen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically. Crystal data for *rac*-BINOL-14DIB cyclic dimer·2CHCl$_3$·2THF: $C_{66}H_{54}Cl_6N_4O_{10}$; $M = 1275.83$; $0.29 \times 0.29 \times 0.11$ mm^3;

monoclinic; space group $P2_1/c$ (no. 14); a = 10.8204(12) Å, b = 35.106(4) Å, c = 8.2849(9) Å; β = 110.005(1)°; V = 2957.2(6) Å^3; Z = 2; ρ_{calcd} = 1.433 gcm^{-3}; μ = 0.356 mm^{-1}; 2θ_{max} = 50.06°; reflections collected: 14141, independent reflections: 5202 (R_{int} = 0.0456), $R_1(I>2\sigma)$ = 0.0500, $wR_2(I>2\sigma)$ = 0.1352; final difference map within +0.440 and -0.427 eÅ^3. CCDC-1952184 (*rac*-BINOL-14DIB cyclic dimer) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational method. Wave-form analysis of SEC curves for determination of the contents of polymers and dimers were performed using Origin 2018 software package (Origin Lab). Molecular mechanics structure optimization was effected using the COMPASS[3] force field implemented in the Discover module of the Material Studio 4.2 (Accelrys) software package with the Fletcher-Reeves[4] conjugate gradient algorithm until the RMS residue went below 0.01 kcal/mol/Å. Molecular dynamic simulation was performed under a constant NVT condition in which the numbers of atoms, volume, and thermodynamic temperature were held constant. Berendsen's thermocouple[5] was used for coupling to a thermal bath. The step time was 1 fs and the decay constant was 0.1 ps. Conformations obtained through MD simulation were saved in trajectory files at every 5 or 10 ps and were optimized by MM simulation.

References

1) G. M. Sheldrick, *SHELXS-2013*, *A program for crystal structure determination*; University of Göttingen, Göttingen, Germany, 2013.

2) G. M. Sheldrick, *SHELXL-2014*, *A program for crystal structure refinement*; University of Göttingen, Göttingen, Germany, 2014.

3) H. Sun, *J. Phys. Chem. B*, 1998, **102**, 7338-7364.

4) R. Fletcher and C. M. Reeves, *Comput. J.*, 1964, **7**, 149-154.

5) H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola and J. R. Haak, *J. Chem. Phys.*, 1984, **81**, 3684-3690.

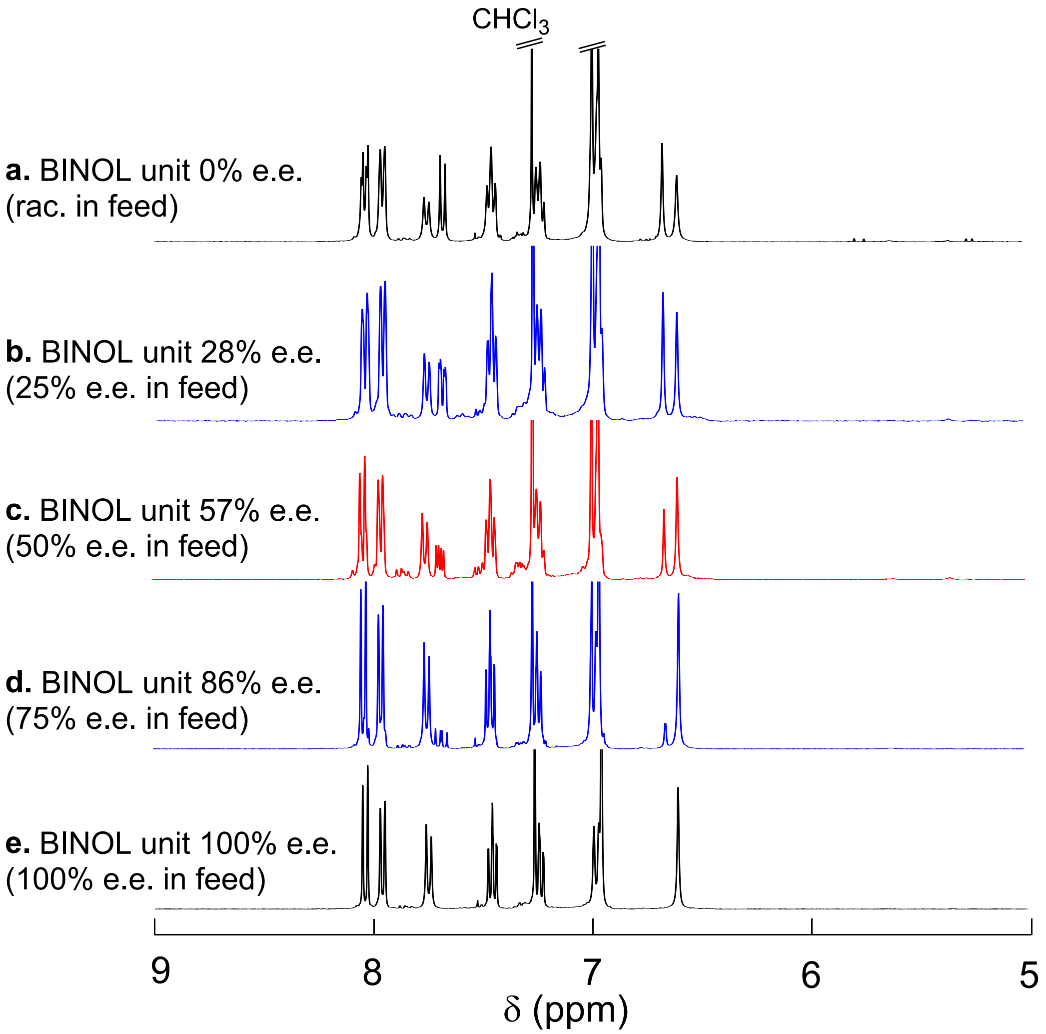


Fig. S1. ^{1}H NMR spectra of BINOL-14DIB cyclic dimers (mixtures of R-R, R-S, S-S dimers) having different e.e.'s of BINOL units prepared at different e.e.'s of BINOL in feed and isolated by preparative SEC: BINOL unit e.e. 0% (a), 28% (b), 57% (c), 86% (d), and 100% (e) (pure R-R cyclic dimer). [400 MHz, r.t., $CDCl_3$]

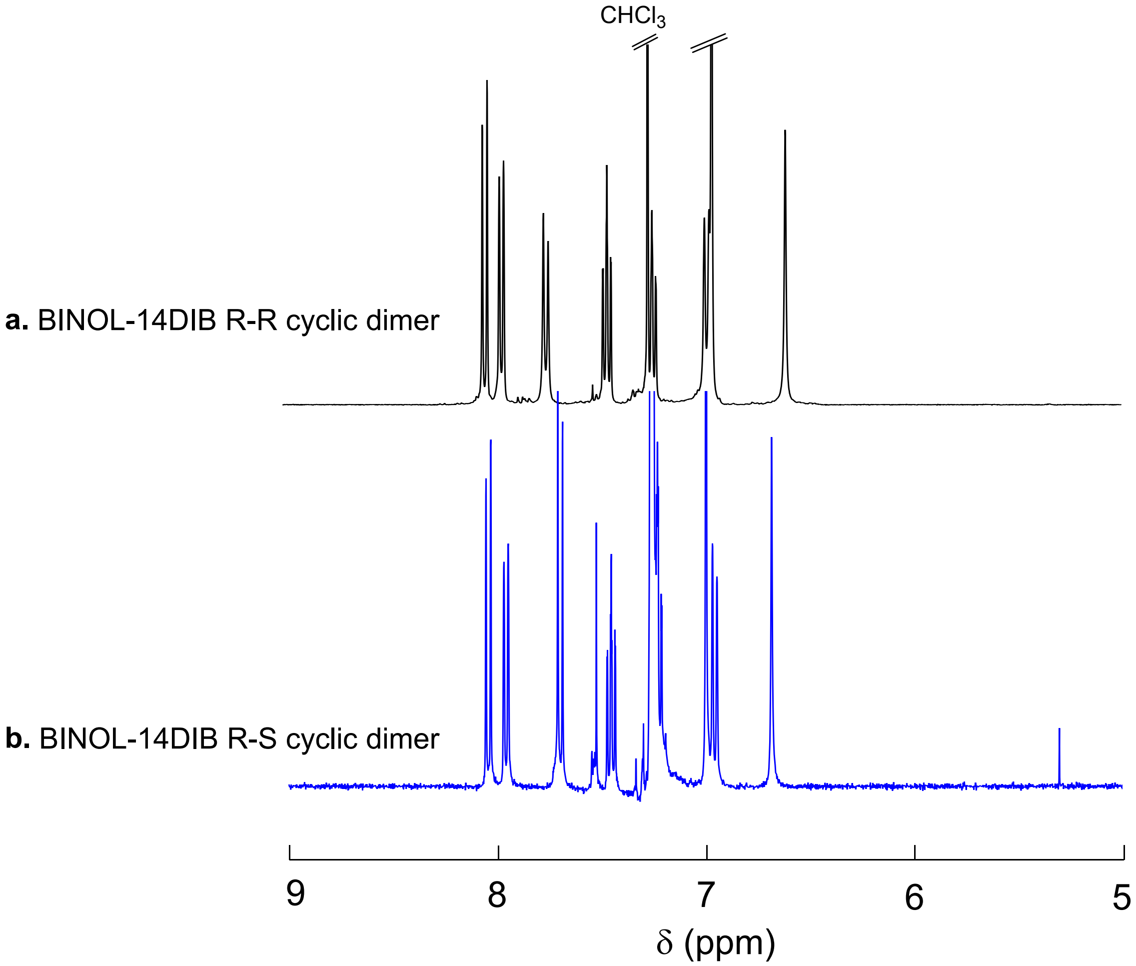


Fig. S2. ^{1}H NMR spectra of BINOL-14DIB cyclic dimers: pure R-R (a) and R-S cyclic dimers. [400 MHz, r.t., CDCl$_3$]

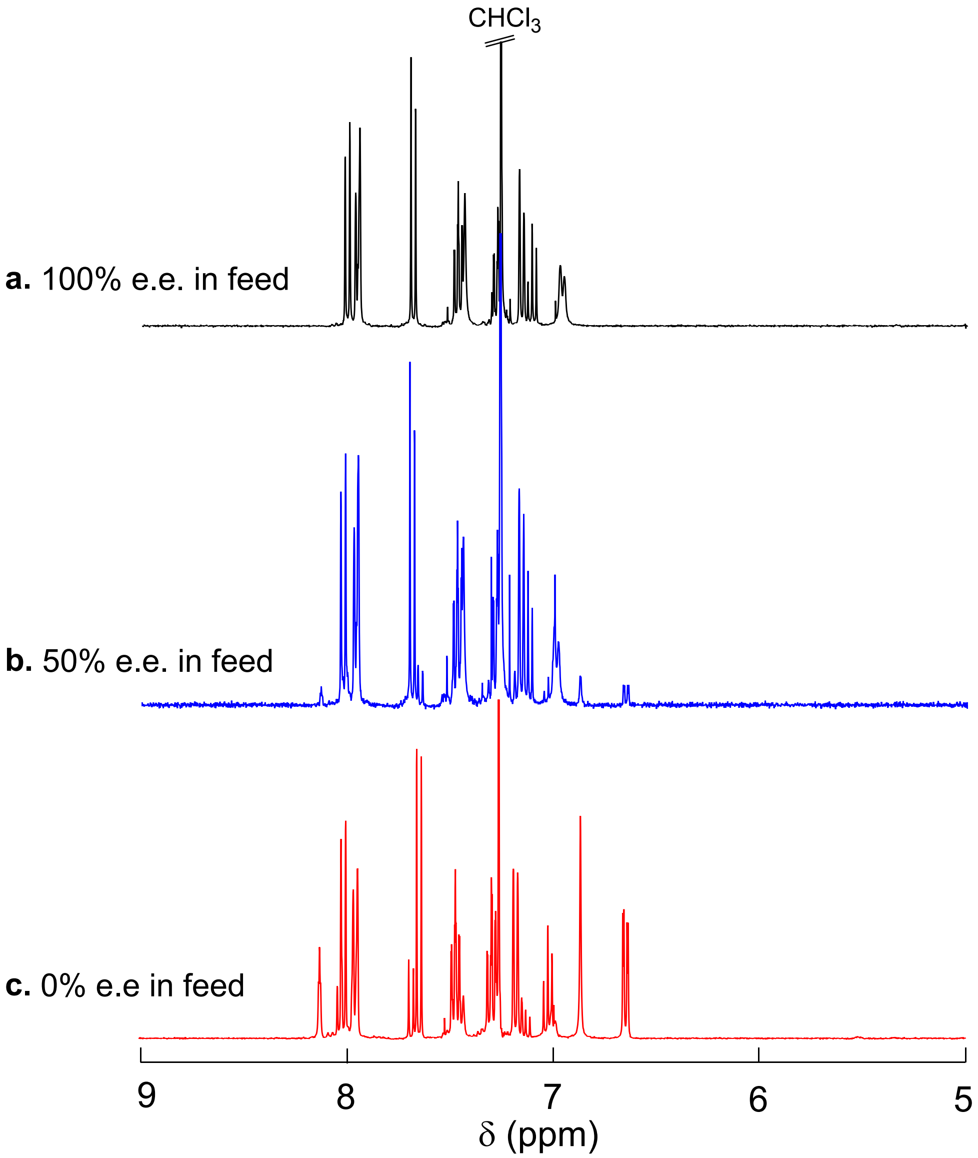


Fig. S3. ^{1}H NMR spectra of BINOL-13DIB linear dimers isolated by preparative SEC from the products at different e.e.'s of BINOL in feed: e.e. in feed 0% (a), 50% (b), and 100% (c). [400 MHz, r.t., $CDCl_3$]

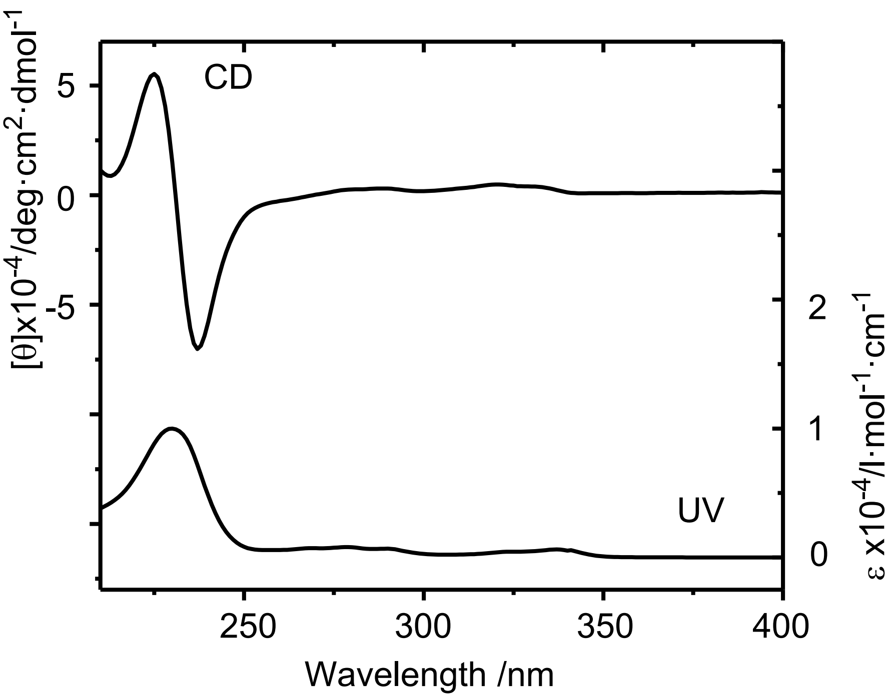
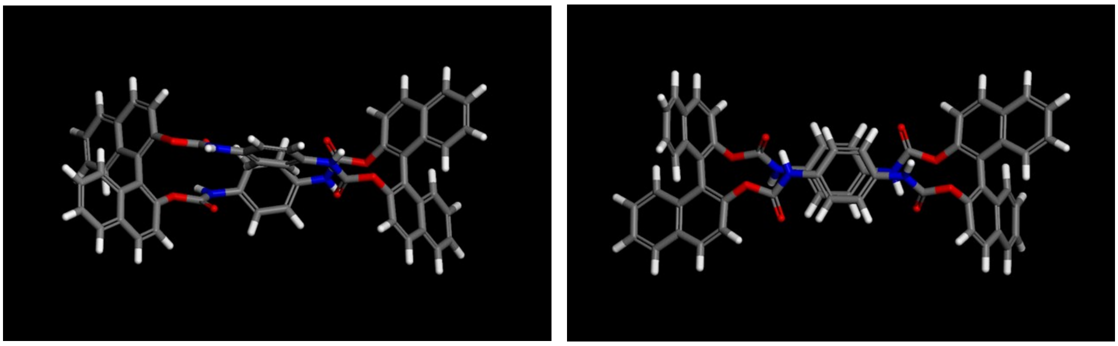
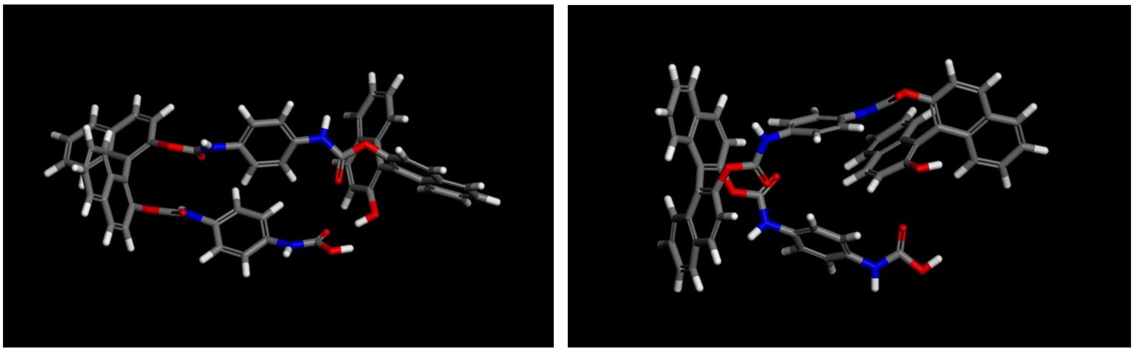


Fig. S4. CD and UV spectra of (R)-BINOL in THF.



A. BINOL-14DIB (R,R)-Cyclic Dimer

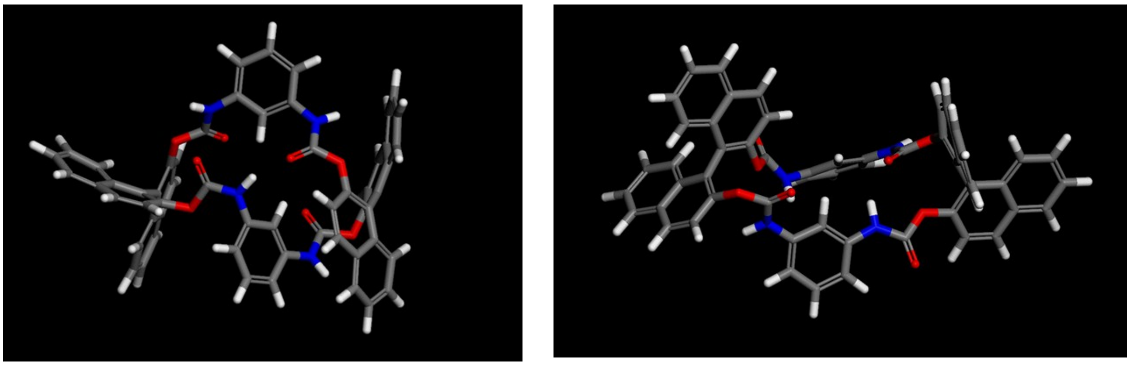
B. BINOL-14DIB (R,S)-Cyclic Dimer



C. BINOL-14DIB (R,R)-Linear Dimer

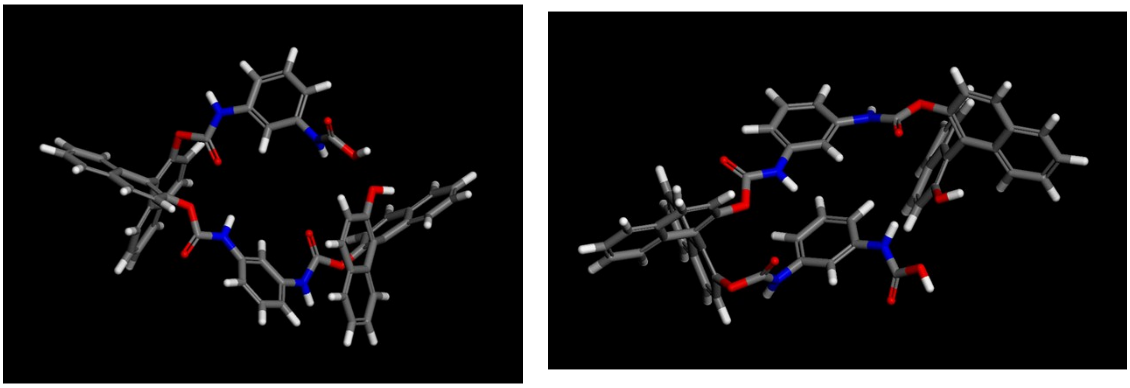
D. BINOL-14DIB (R,S)-Linear Dimer

Fig. S5. Structures of (R,R)-cyclic dimer (A), (R,S)-cyclic dimer (B), (R,R)-linear dimer (C), and (R,S)-linear dimer (D) of the BINOL-14DIB system obtained by simulation. A and B were obtained through MM optimization of the corresponding crystal structures, and C and D were obtained by MD simulation for 3 nsec at 297K followed by MM optimization using COMPASS force field. Total steric energies are 409.5 kcal mol^{-1} (A), 390.69 kcalmol^{-1} (b), 288.56 kcalmol^{-1} (C), and 278.47 kcalmol^{-1} (D).



A. BINOL-13DIB (R,R)-Cyclic Dimer

B. BINOL-13DIB (R,S)-Cyclic Dimer



C. BINOL-13DIB (R,R)-Linear Dimer

D. BINOL-13DIB (R,S)-Linear Dimer

Fig. S6. Structures of (R,R)-cyclic dimer (A), (R,S)-cyclic dimer (B), (R,R)-linear dimer (C), and (R,S)-linear dimer (D) of the BINOL-13DIB system obtained by MD simulation for 3 nsec at 297K followed by MM optimization using COMPASS force field. Total steric energies are 381.9 kcal mol^{-1} (A), 396.1 kcal mol^{-1} (B), 262.3 kcal mol^{-1} (C), and 279.0 kcal mol^{-1} (D).

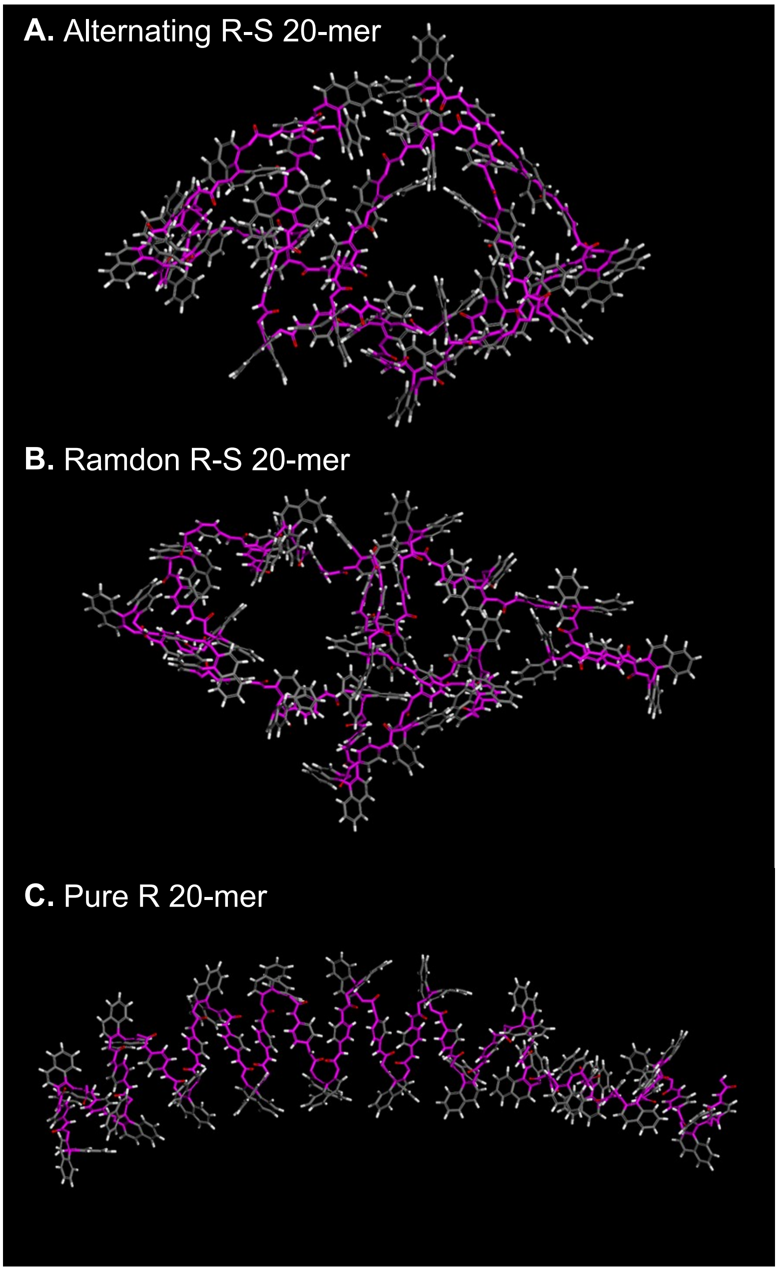
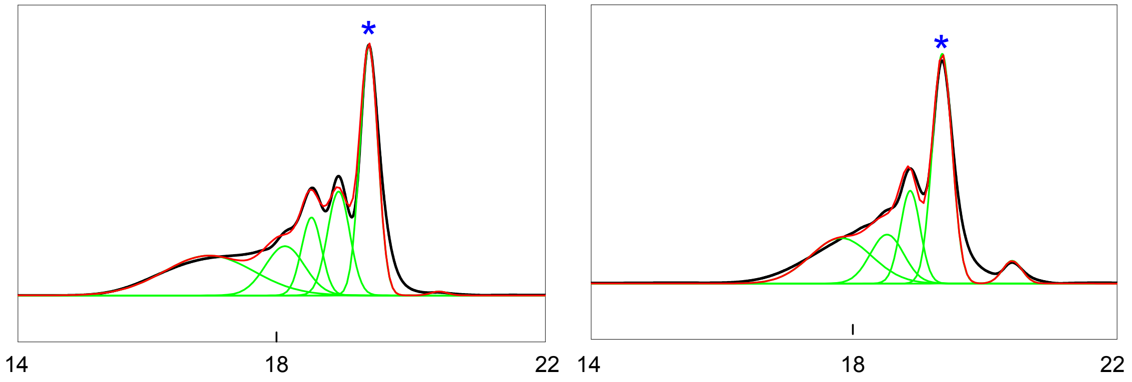
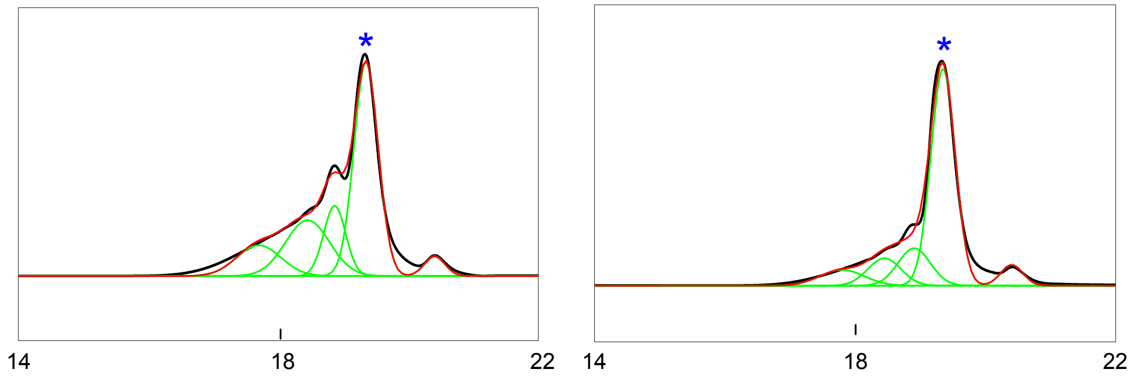


Fig. S7. Conformations of 20-mer chains of poly(BINOL-*alt*-14DIB) having alternating (R)-BINOL and (S)-BINOL units (a), randomly distributed (R)-BINOL and (S)-BINOL units (b) and only (R)-BINOL units obtained by MD simulations at 297K for 14-16 ns (NVT) using COMPASS force field. Total steric energies are 2826 kcal mol^{-1} (A), 2709 kcal mol^{-1} (B), and 2474 kcal mol^{-1} (C).



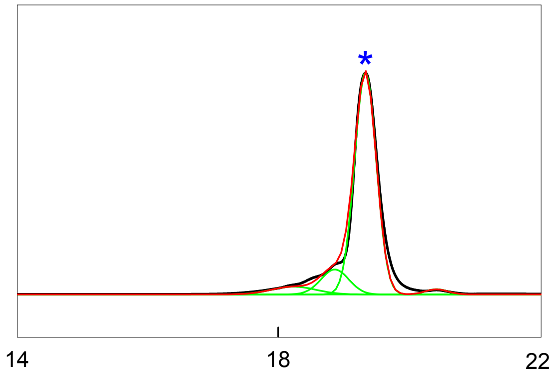
A. (R)-BINOL 100% e.e. in feed

B. (R)-BINOL 75% e.e. in feed



C. (R)-BINOL 50% e.e. in feed

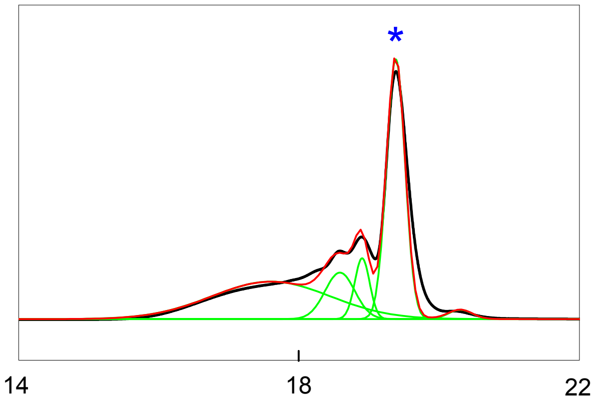
D. (R)-BINOL 75% e.e. in feed



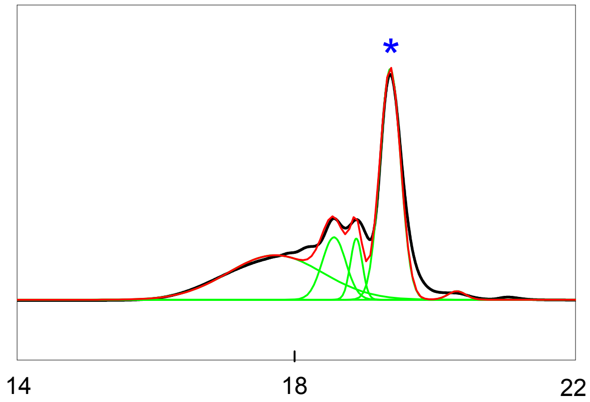
E. BINOL 0% e.e. in feed

Fig. S8. Wave-form analysis of SEC curves of poly(BINOL-*alt*-14DIB) to determine the contents of cyclic dimer. Black curves are experimental SEC traces, green curves are deconvoluted Gaussian functions, and red curves are regenerated, entire SEC traces obtained by the addition of all deconvoluted functions. * denotes cyclic dimer peaks.

A. (R)-BINOL 100% e.e. in feed



B. (R)-BINOL 50% e.e. in feed



C. BINOL 0% e.e. in feed

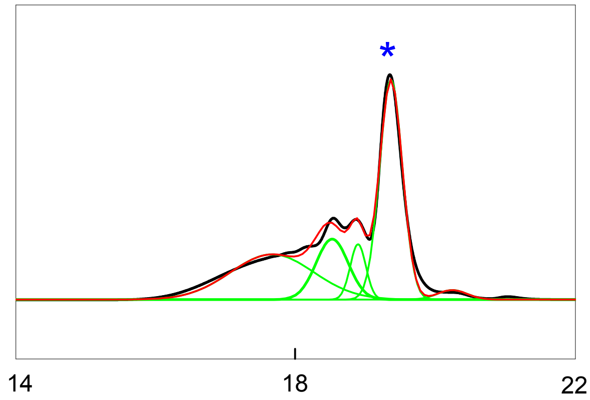


Fig. S9. Wave-form analysis of SEC curves of poly(BINOL-*alt*-13DIB) to determine the contents of linear dimer. Black curves are experimental SEC traces, green curves are deconvoluted Gaussian functions, and red curves are regenerated, entire SEC traces obtained by the addition of all deconvoluted functions. * denotes linear dimer peaks.

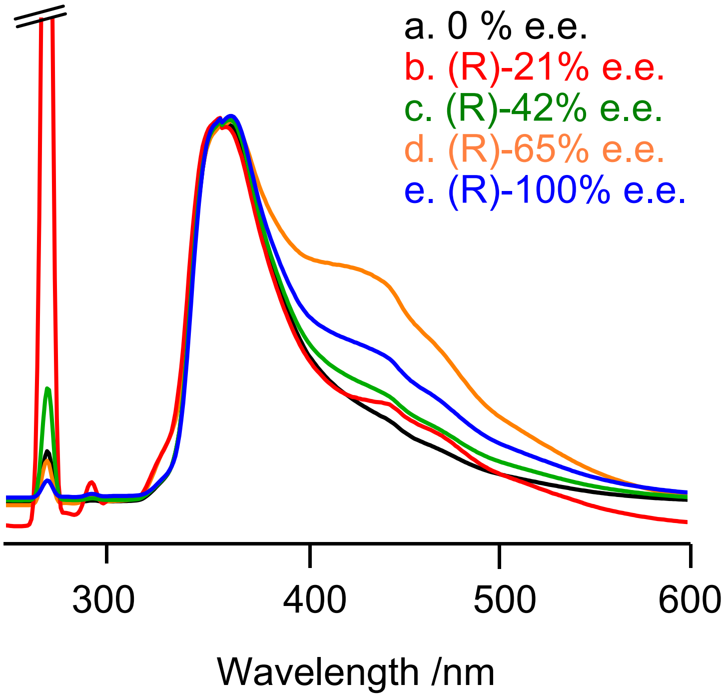


Fig. S10. Fluorescence spectra of poly(BINOL-*alt*-14DIB)s having different e.e.'s of BINOL units in a THF solution: **a.** (*R*)-21% e.e., M_n 2920 (25% e.e. of (*R*)-BINOL in feed), **b.** (*R*)-42% e.e., M_n 2740 (50% e.e. of (*R*)-BINOL in feed); **c.** (*R*)-65% e.e., M_n 2870 (75% e.e. of (*R*)-BINOL in feed); **d.** (*R*)-100% e.e., M_n 3520; **e.** (*R*)- 0% e.e., M_n 2320. [1-cm cell, conc. 1.0 x 10^{-3} M, λ_{ex} 270 nm]

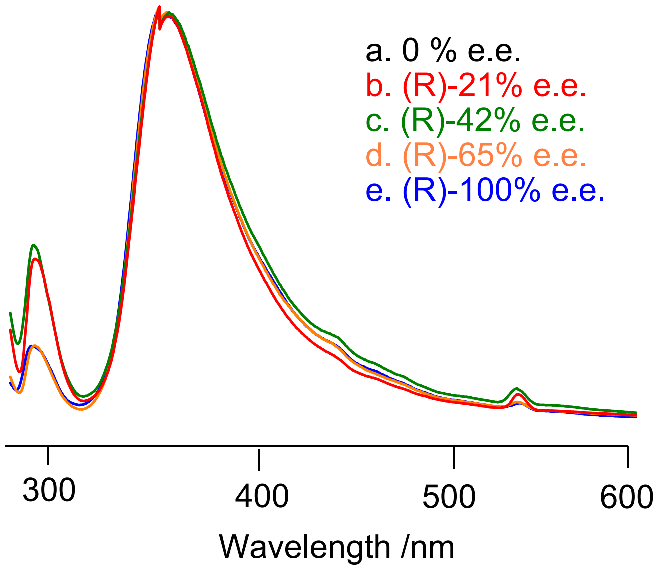
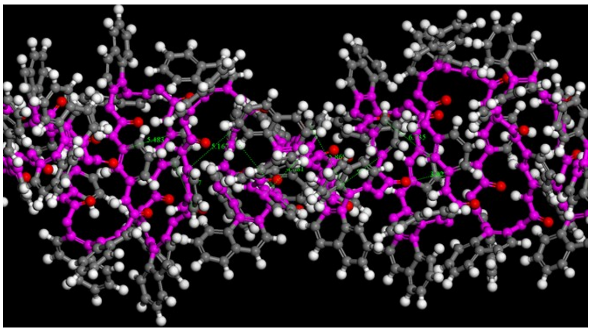
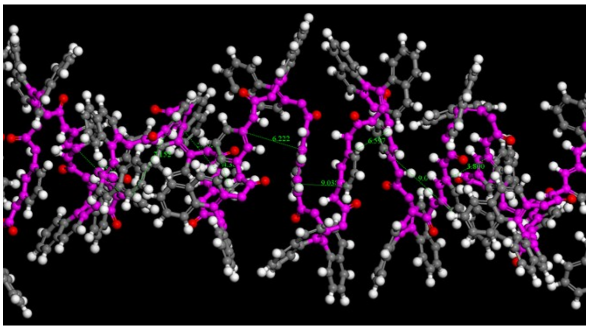


Fig. S11. Fluorescence spectra of poly(BINOL-*alt*-14DIB)s having different e.e.'s of BINOL units in a cast film: **a.** (*R*)-21% e.e., M_n 2920 (25% e.e. of (*R*)-BINOL in feed), **b.** (*R*)-42% e.e., M_n 2740 (50% e.e. of (*R*)-BINOL in feed); **c.** (*R*)-65% e.e., M_n 2870 (75% e.e. of (*R*)-BINOL in feed); **d.** (*R*)-100% e.e., M_n 3520; **e.** (*R*)- 0% e.e., M_n 2320.

A. 9/1-Helix



B. 8/1-Helix



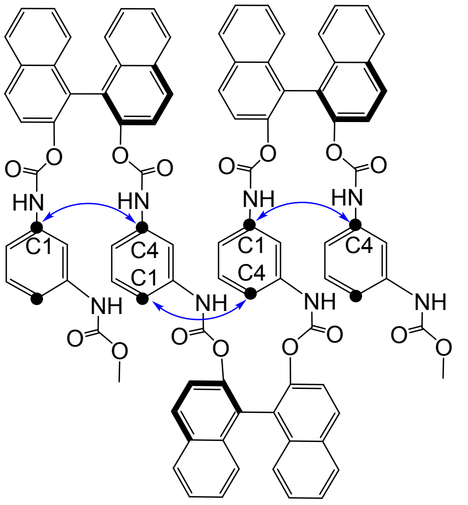


Fig. S12. Optimized conformations of poly((R)-BINOL-*alt*-13DIB) 20-mer, 9/1-helix (A) and 8/1-helix (B) with measured distances between between C1 and C4 of neighboring benzene-1,3-diyl units. The central nine units starting from the sixth one form a terminal were selected for distance measurements to avoid terminal effects. The averaged distances were 5.66 Å in A and 6.37 Å in B.

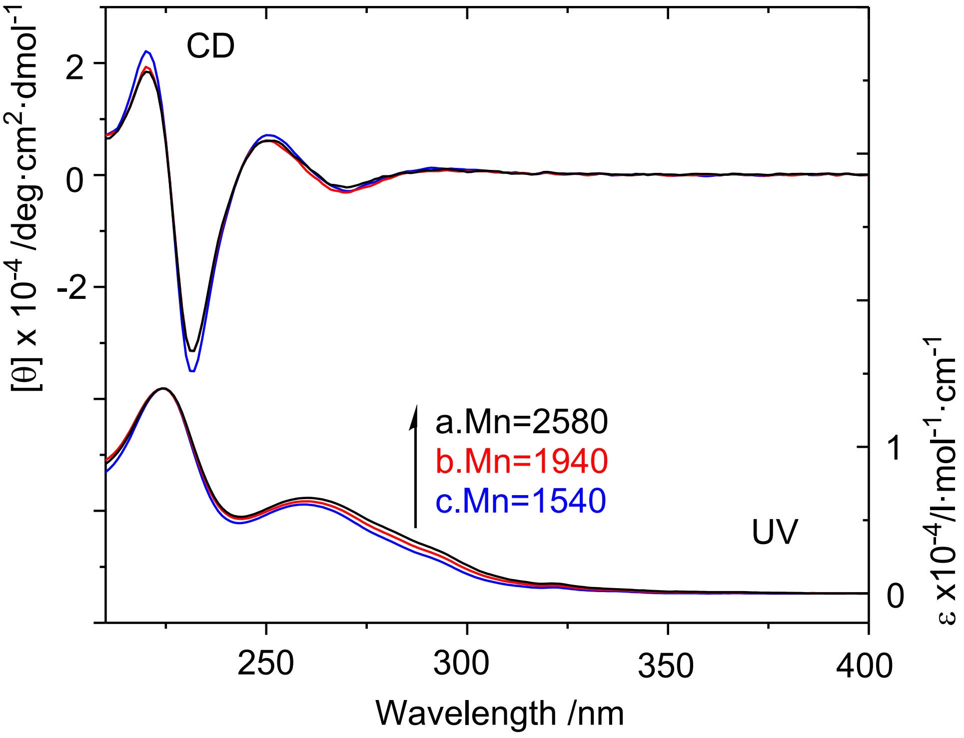


Fig. S13. UV and CD spectra of poly(BINOL-*alt*-14DIB)s of M_n 2580 (a), 1940 (b) and 1540 (c) obtained at 50% e.e. of (*R*)-BINOL in feed in THF solution. The samples were separated from the product of reaction at [BINOL] = [14DIB] = -0.154 M at room temperature for 24 h.

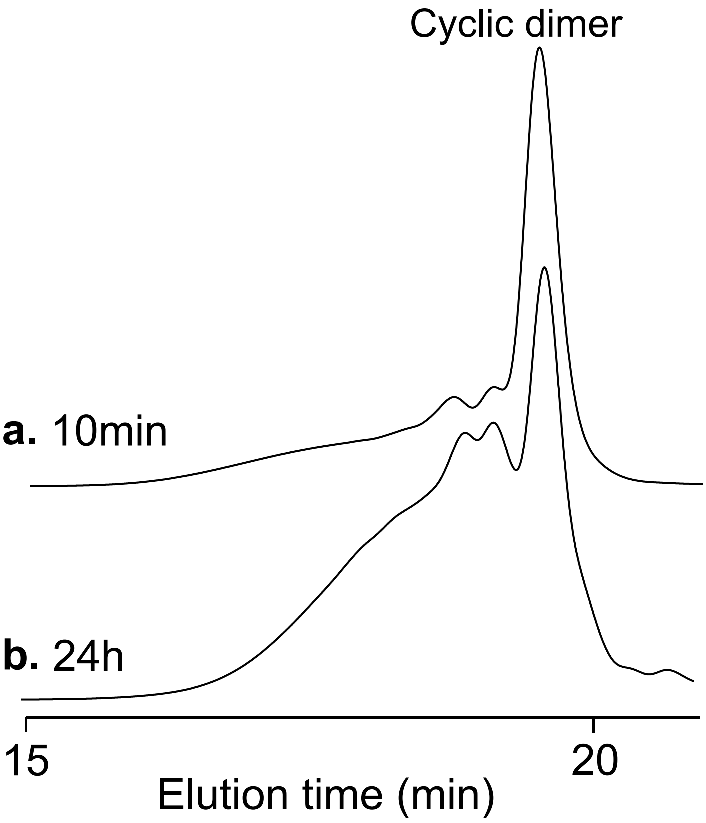


Fig. S14. SEC profiles of polymerization products obtained from 14DIB and (*R*)-BINOL at 50% e.e in 10 min (A) and 24 h (B) of reaction at [BINOL] = [14DIB] = 0.154 M at room temperature. [detection by UV at 254 nm].

In both cases, BINOL monomer was consumed at a high conversion ratio. The product obtained in 10 min consists mostly of the cyclic dimer while the one in 24 h contains a higher amount of polymer fractions, indicating that the cyclic dimer is formed first and then the polymer is formed by the intra-chain combination of shorter, linear chains (chain growth).

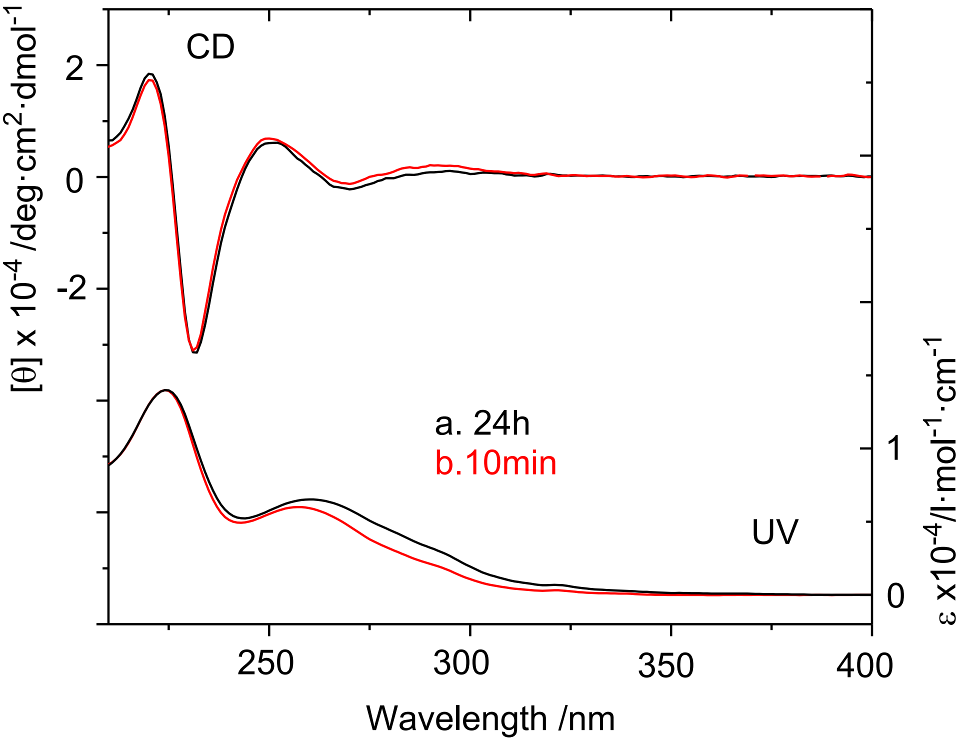
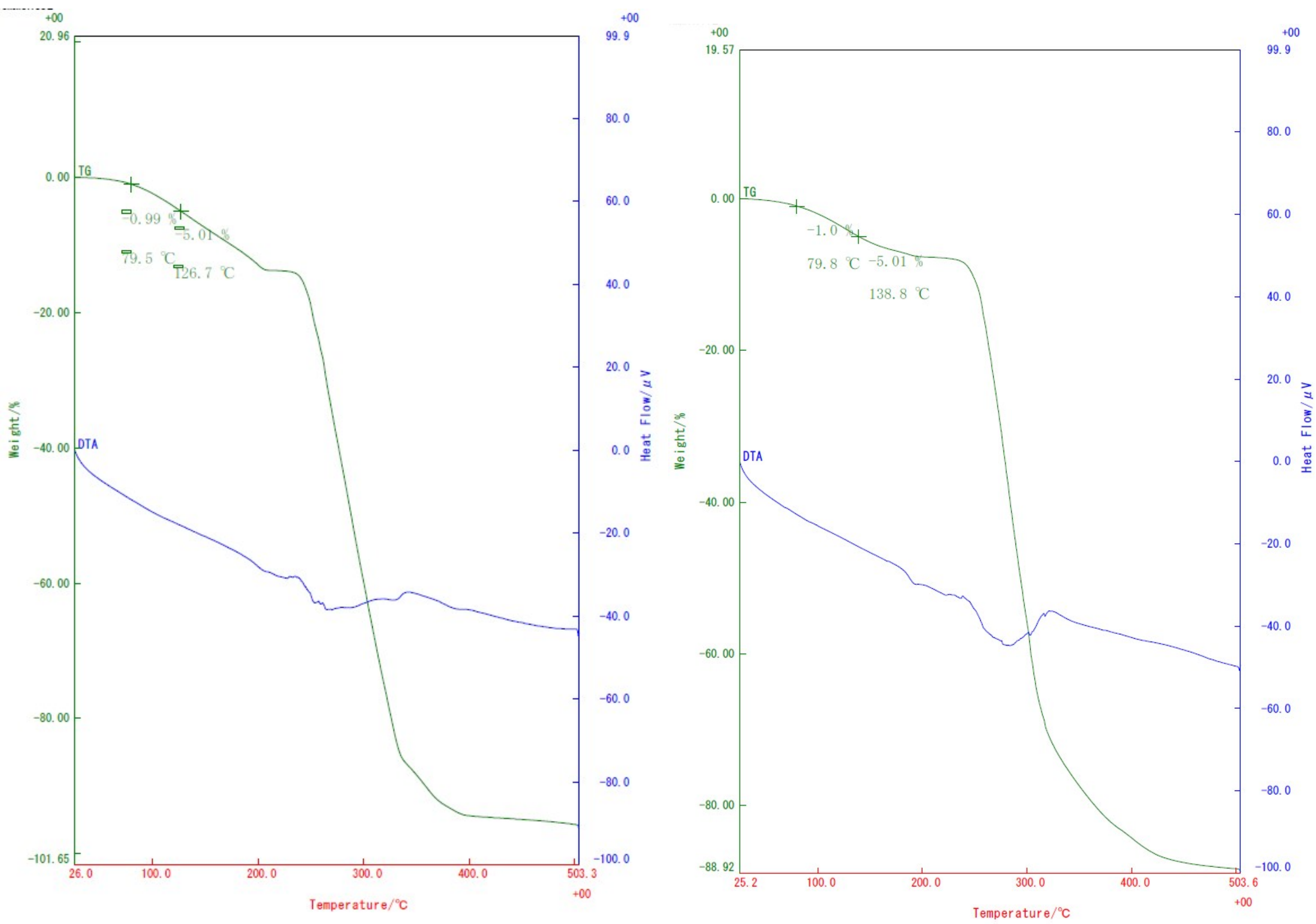
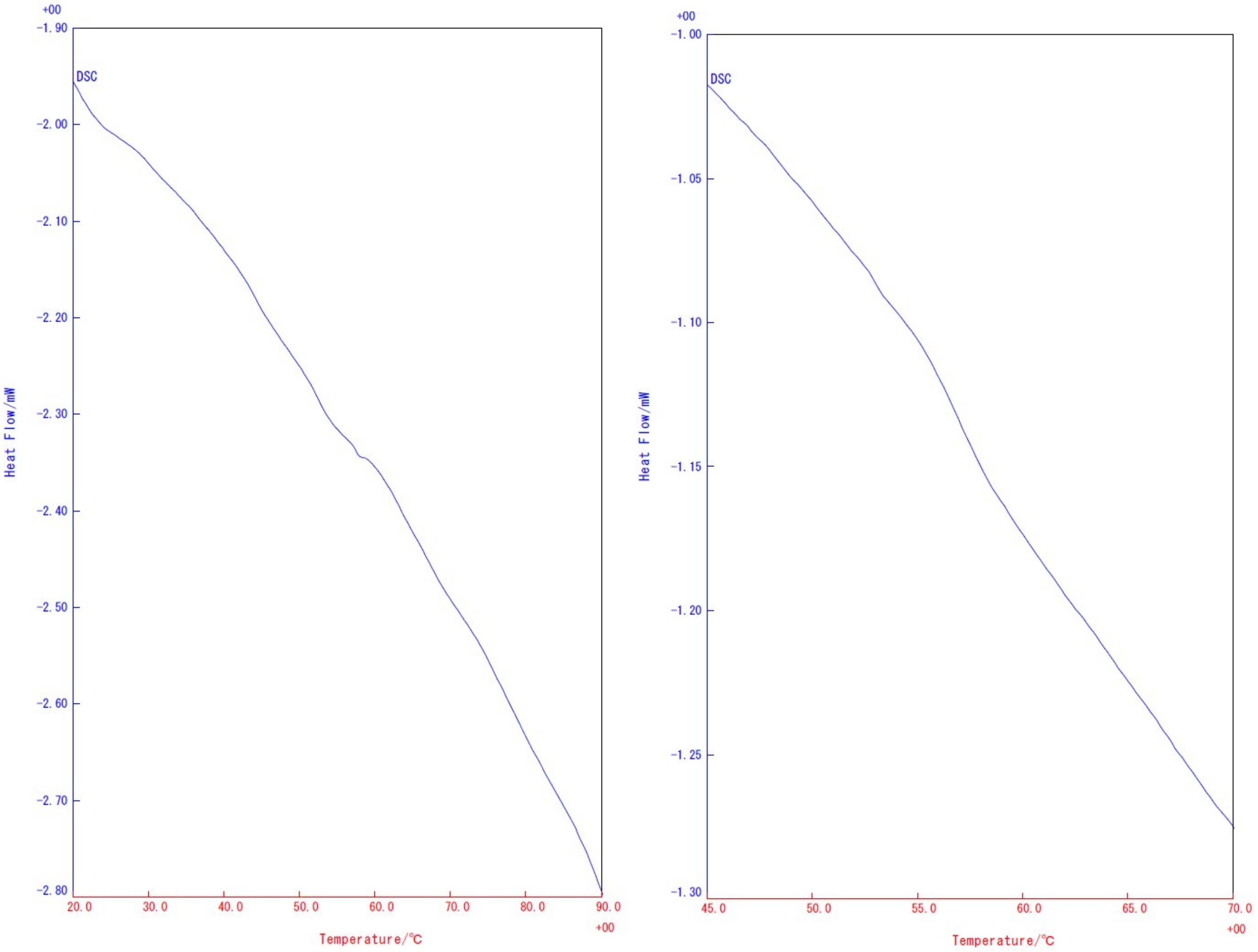


Fig. S15. UV and CD spectra of poly(BINOL-*alt*-14DIB)s obtained in 24 hn (a) and 10 min (b) of polymerization at 50% e.e. of (*R*)-BINOL in feed in THF solution.


A. Poly(BINOL-*alt*-14DIB)

B. Poly(BINOL-*alt*-13DIB)

Fig. S16. DT-TGA profiles of poly(BINOL-*alt*-14DIB) (M_n 2720) (A) and poly(BINOL-*alt*-13DIB) (M_n 2460) (B) obtained at 100% e.e. of (*R*)-BINOL in feed [heating scan rate: 10 deg/min].

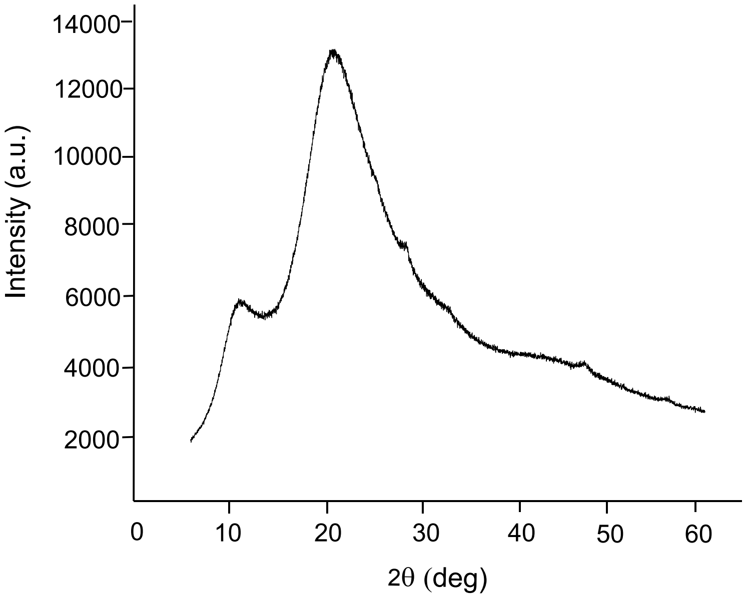


A. Poly(BINOL-*alt*-14DIB)

B. Poly(BINOL-*alt*-13DIB)

Fig. S17. DSC profiles of poly(BINOL-*alt*-14DIB) (M_n 2720) (A) and poly(BINOL-*alt*-13DIB) (M_n 2460) (B) obtained at 100% e.e. of (*R*)-BINOL in feed [2nd heating scan at 10 deg/min].

A. Poly(BINOL-*alt*-14DIB)



B. Poly(BINOL-*alt*-13DIB)

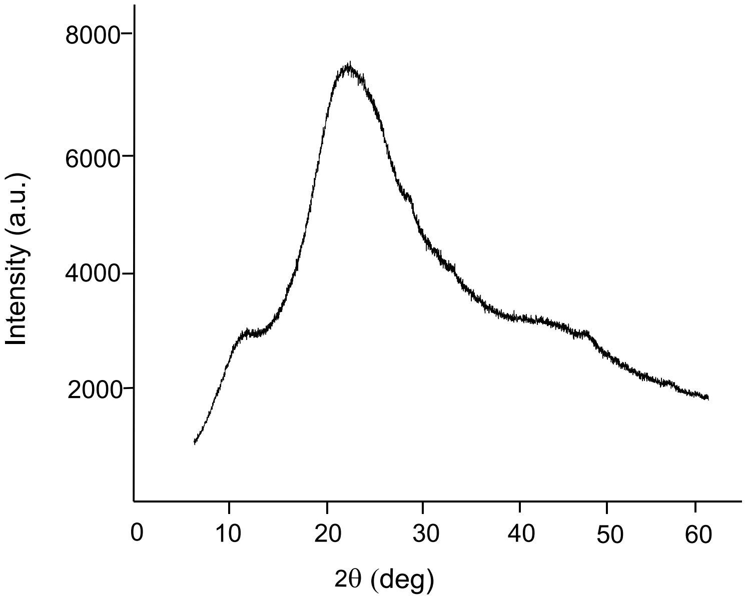


Fig. S18. WAXD profiles of poly(BINOL-*alt*-14DIB) (M_n 2720) (A) and poly(BINOL-*alt*-13DIB) (M_n 2460) (B). [RIGAKU Miniflex diffractometer, CuKa, 30 KV, 10 mA, scan speed 1.25 degree/min, step 0.01 degree]